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The influence of HfO_2 additives on the optical properties of Nd^{3+}-doped Y_2O_3 ceramics

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Transparent yttria ceramics were fabricated by sintering a mixture of 1 at.% Nd:Y_2O_3 and HfO_2 nanopowders produced by laser synthesis method. The best transmittance was 80.96% at the wavelength of λ=1080 nm in 6 mol.% HfO_2 doped sample (1.5 mm thick). The additives of hafnium broaden both pumping and luminescence bands of Nd^{3+} ion in yttria ceramics. The luminescence intensity of $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition was little affected by hafnium concentration. The effective lifetime of $^4F_{3/2}$ level in Nd:Y_2O_3 ceramics enhanced by 30% at 10 mol.% HfO_2 doping concentration and the decay kinetics of laser transition attains Förster's behavior.

1 Introduction Doping of yttria ceramics with HfO_2 additives leads to disordering of crystal structure and changing of optical properties of material [1,2]. For instance, pore-free yttria ceramics were obtained at the concentration of HfO_2 2,6 mol.%. The absorption spectral width of such ceramics was close to that of a Nd:Y_2O_3 single crystal and emission bandwidth was higher than of Nd:YAG (3,4 and 0,7 nm, respectively).

It is known [3,4] that disordering of ceramics crystal structure leads to broadening of spectral band of laser transition that is suitable for ultra-short pulse laser generation. Earlier it was shown that the greatest broadening is reached at doping of ceramics by heterovalent ions. Unfortunately, our efforts to receive the laser oscillation in highly transparent ZrO_2-doped Nd:Y_2O_3 ceramics with disordered crystal structure were not successful [5,6]. It was caused by reducing of lifetime and luminescence intensity (up to 2 times) of upper laser level and by broadening of spectral band of laser transition that also reduces the gain coefficient.

The purpose of this paper is to report on fabrication process and optical characteristics such as transmission and luminescence spectra, effective lifetime, quantum efficiency and quenching kinetics of $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition in Nd:Y_2O_3 ceramics doped by HfO_2 additives.

2 Experimental The 1 at.% Nd:Y_2O_3 and HfO_2 nanopowders were produced using laser synthesis method [7] which involves evaporation of solid target by pulse-periodical CO_2-laser and eventual condensation of vapor in air flow. The laser targets of Nd:Y_2O_3 and HfO_2 were prepared from coarse commercial powders with purity of >99.99% and initial particle sizes of 1-20 μm by pressing at 10 MPa and pre-sintering at 1300 °C for 5 h. After pre-sintering the laser targets were 60 mm in diameter and 19 mm in thickness.

The main laser parameters at the synthesis were as follows: average power P=550 W, peak power P_p=8-9 kW, half-height duration τ_l=330 μs, pulse repetition rate f=500 Hz, output rate 28 and 21 g/hour for Nd:Y_2O_3 and HfO_2 nanopowders, respectively.

At the laser synthesis of Y_2O_3-based nanopowders the particles are produced in metastable monoclinic phase (XRD on D/Max-2200V/PC diffractometer, Fig. 1a). The transformation of monoclinic phase in a main cubic is accompanied by substantial growth of elementary cell volume. Therefore, in order to avoid destruction of ceramic sample during sintering this phase transformation was performed in advance by annealing of Nd:Y_2O_3 nanopowder at 1000 ºC for 30 min. XRD analysis of annealed nanopowder on D8 Discover diffractometer has shown that

the content of the cubic phase at these annealing conditions is equal to 100% (Fig. 1b). According to the BET analysis the specific surface area of the Nd:Y_2O_3 particles after annealing was 17.92 m^2/g, i.e. the size of particles increased from 12 to 69 nm.

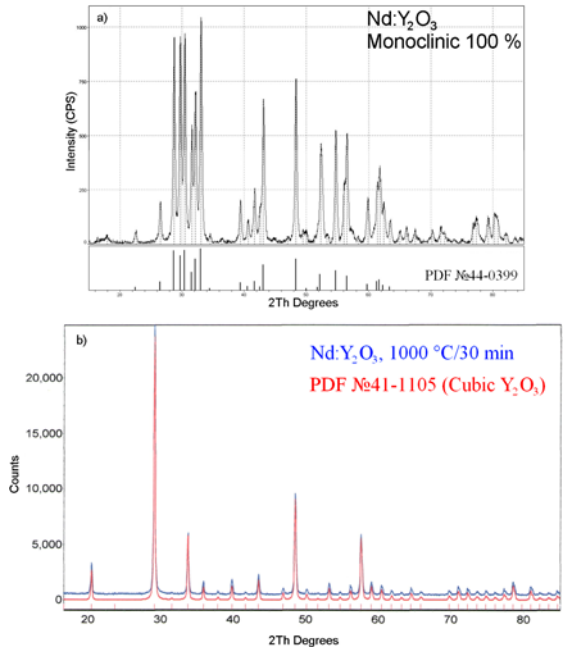

Figure 1 XRD of 1 at.% Nd:Y_2O_3 nanopowder before and after annealing at 1000 ºC for 30 min.

Then HfO_2 and annealed Nd:Y_2O_3 nanopowders were mixed in demanded composition in a plastic bottle with ethanol and YSZ balls for 48 h. The dried mixture was uniaxially pressed into Ø15 mm pellets at 133 MPa. The pellets then were sintered at 1900 °C for 20 h in a high temperature vacuum furnace GERO HTK-8W/22-1G-HV under $3 \cdot 10^{-5}$ mbar vacuum during holding. The sintered samples were annealed in air at 1400 °C for 2 h to eliminate the oxygen vacancies.

The transmission spectra of polished ceramic samples with the thickness of ~1.5 mm were recorded using dual-beam spectrophotometer Shimadzu UV-1700. The emission spectra and lifetime of $^4F_{3/2}$ level were measured using ATC-type laser light-emitting diode with power of 3 W at a wavelength of λ_p=808±3 nm in combination with the recording device consisting of the FD-24K photodiode and the Tektronix TDS 520 oscilloscope. All measurements were carried out at room temperature.

3 Results and discussion

3.1 Optical properties The photo of synthesized samples after polishing is shown in Fig. 2. It can be seen that undoped and 1 mol.% HfO_2 doped samples are opaque at these sintering conditions but transparency grows with increase of HfO_2 concentration.

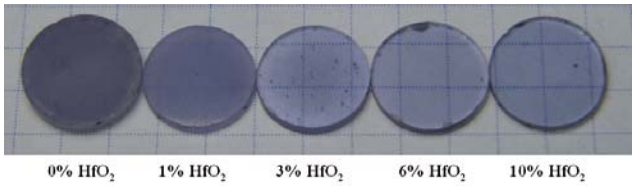

Figure 2 The photo of synthesized samples.

Figure 3 shows transmission spectra of samples doped with different concentration of HfO_2. The sample with 6 mol.% HfO_2 has a higher transmittance – 80.96% at the wavelength of λ=1080 nm. Transmittance of 10 mol.% doped sample is less than 6 mol.% probably due to the formation of excessive secondary phase near grain boundaries.

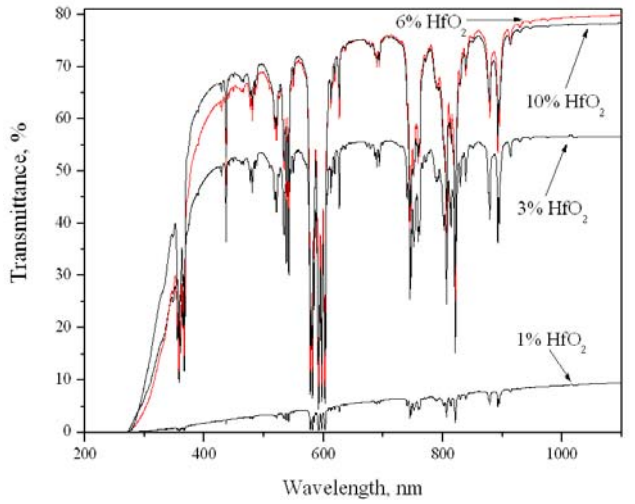

Figure 3 Transmission spectra of HfO_2 doped samples.

Figure 4 shows the transmission spectra of samples at the pumping wavelengths λ=803-808 nm. To demonstrate the broadening of pumping band with increase of HfO_2 concentration we used transparent Nd:Y_2O_3 ceramic sample without hafnium prepared in optimal sintering conditions.

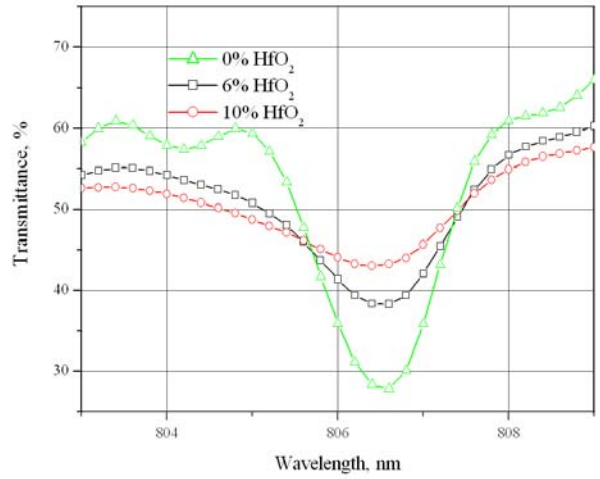

Figure 4 Transmission spectra of samples at the pumping wavelengths.

The effective lifetimes of $^4F_{3/2}$ level were determined from the oscilloscope patterns of luminescence decaying (inset of Fig. 5 shows oscillogram of HfO_2-undoped sample). Figure 5 shows the effective lifetime of the $^4F_{3/2}$ level in $Nd:Y_2O_3$ ceramics as a function of HfO_2 concentration. The effective lifetimes of 0, 1, 3, 6 and 10 mol.% HfO_2 doped samples were 190, 210, 220, 240 and 255 μs, respectively. So the higher hafnium concentration enhanced the effective lifetime by 30%.

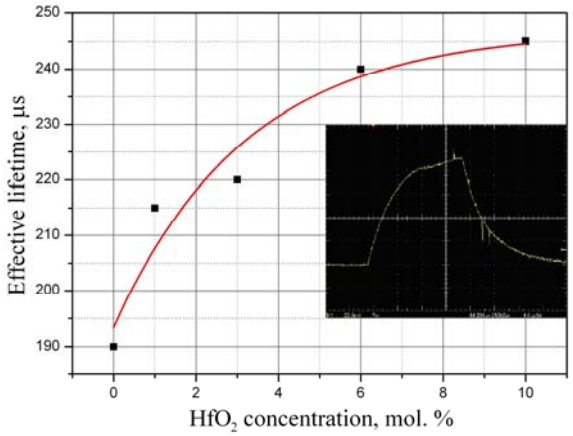

Figure 5 Effective lifetime of $^4F_{3/2}$ level in $Nd:Y_2O_3$ ceramics versus HfO_2 concentration. Inset shows the experimental oscillogram of luminescence in HfO_2-undoped sample.

It is interesting to note that the measured effective lifetime in prepared ceramics without HfO_2 (190 μs) is less than reported lifetime in similar single-crystal (255 μs) [8] and ceramics (220 μs) [9]. It is probably connected with the presence in our ceramics some kind of intrinsic defects such as bonded radicals $^{O}_{O}>Y=O$, Nd^{3+} ions located in distorted positions of crystal lattice, surface defects and dislocations.

According to the emission spectra (Fig. 6), doping with HfO_2 leads to a broadening of spectral bands in the λ=1040–1090 nm region due to Stark-splitting of $^4F_{3/2}$ and $^4I_{11/2}$ levels. In this wavelengths range two lines overlap and form a wider band with total width of 37 nm at 20% level of maximum luminescence intensity.

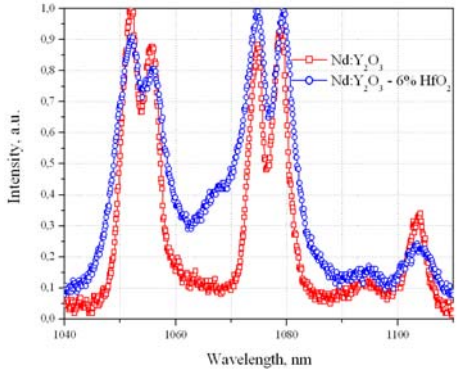

Figure 6 Emission spectra of undoped and 6 mol.% HfO_2 doped $Nd:Y_2O_3$ ceramics.

The relative quantum efficiency of HfO_2 doped samples regarding $Nd:Y_2O_3$ sample was measured by cutting of luminescence radiation under the same angle and registration using photodiode and oscilloscope. According to received data the luminescence intensity of HfO_2 doped ceramics decreases by 5-10%.

3.2 Processing of radiative decay curves Received $^4F_{3/2}$ emission decay curves were approximated by Eq. (1),

$$I(t) = I_0 \exp\left(-\frac{t}{\tau_r} - \sqrt{\frac{t}{\tau_f}}\right), \quad (1)$$

where τ_r and τ_f are the characteristic times of radiative decay and Förster's quenching, respectively [10]. Approximation was performed using properly Mathcad function. The results of processing are given in Table 1.

Table 1 Results of processing

Concentration of HfO_2, mol.%	0	1	3	6	10
τ_r, μs	311	500	650	550	715
τ_f, μs	978	277	203	329	179

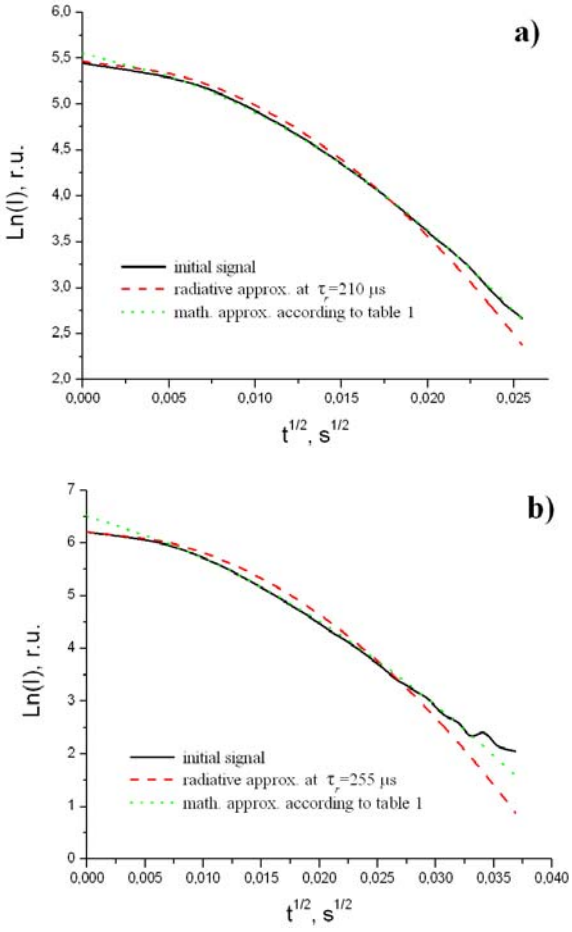

Figure 7 Luminescence kinetics in $Nd:Y_2O_3$ (a) and $Nd:Y_2O_3$-HfO_2 (b) samples.

Without HfO_2 the emission decay behavior is almost radiative or close to $\exp(-t/\tau_r)$ and Förster's part is negligible (Fig. 7a). It can be seen that deviation of initial signal from radiative curve at τ_r=210 μs is insignificant.

The value of τ_r=210 μs most close approaches to experimental curve and to the value given in Fig. 5 (190 μs). The decay behavior becomes Förster's, i.e.

$$\exp\sqrt{\frac{t}{\tau_f}}\ , \qquad (2)$$

(Fig. 7b) when the concentration of HfO_2 is 1 mol.%. In this case the difference between experimental and closest radiative curve (at τ_r=255 μs) is more considerable. The further increasing of hafnium concentration does not qualitatively affect behavior although Förster's part becomes larger i.e. τ_f decreases and τ_r grows with increase of concentration (Table 1). Exception of this tendency is 6 mol.% doped sample but the reasons of given fact while not clear.

These results suggest the presence of some defects which are acceptors for $^4F_{3/2}$ level of Nd^{3+} ion in Y_2O_3 ceramics. Further research is in progress to clarify the kind of acceptors.

4 Conclusions Transparent ceramics of 1 at.% Nd:Y_2O_3 doped with different concentration of HfO_2 were fabricated from nanopowders produced by laser method. The higher transmittance was 80,96% at λ=1080 nm in 6 mol.% HfO_2 doped Nd:Y_2O_3 sample. Additives of HfO_2 broaden the emission bandwidths of Nd^{3+} ($^4F_{3/2}\rightarrow{}^4I_{11/2}$) transition up to 37 nm at 20% level of maximum luminescence intensity. The effective lifetime of $^4F_{3/2}$ level grows up to 30% when concentration of HfO_2 is 10 mol.%. The luminescence intensity of $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition was little affected by hafnium concentration.

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